*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

# SELECTIVE PHENYLATION OF OLEFINS WITH TRIPHENYLALUMINUM

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(Received July 31st, 1969; in revised form October 14th, 1969)

## SUMMARY

The arylation of selected olefinic types by aluminum aryls was surveyed, as to feasibility and stereoselectivity, by an examination of the behavior of triphenylaluminum toward 1,1-diphenylethylene, 1-octene, *exo*-5-phenylbicyclo[2.2.1]hept-2-ene, bicyclo[2.2.1]hepta-2,5-diene and indene, respectively. The first four substrates underwent phenyl–aluminum bond addition with a reactivity increasing in the order given; but indene suffered only metallation. The variation in olefin reactivity, the stereo- and regio-specificity, and the metallation of indene and *cis*-stilbene seem to best explained by means of electrophilic attack by aluminum on carbon, proceeding through a $\pi$- or $\sigma$-complex.

## INTRODUCTION

The original observation by Ziegler and coworkers[1] of the addition of aluminum alkyls to ordinary olefins has proved to be a seminal discovery in the development of industrial oligomerization and polymerization processes[2]. Subsequent research has shown that similar alkylation[3] and arylation[4,5] reactions can be realized with acetylenic compounds by means of the appropriate organoaluminum reagent. Little is known, however, about the feasibility of arylating ordinary olefins with arylaluminum compounds. Triphenylaluminum has been added in a 1,4-manner to 1,3-diphenyl-1-propen-3-one to yield, upon hydrolysis, 1,3,3-triphenyl-1-propanone[6], but information on the orientation and stereochemistry of such additions to simple and conjugated olefinic hydrocarbons is lacking.

In order to provide information on the arylation of olefins, the behavior of a typical arylaluminum reagent, triphenylaluminum, was examined, in turn, toward a terminal olefin (1-octene), toward a stable conjugated olefinic (1,1-diphenylethylene), and toward reactive cycloolefins able to reveal the stereochemistry of addition (indene and bicyclo[2.2.1]hepta-2,5-diene).

## EXPERIMENTAL

The preparation, manipulation and reactions of triphenylaluminum were performed under an atmosphere of oxygen- and moisture-free nitrogen in general accordance with published procedures[4].

Benzene and toluene used as reaction solvents were of the highest purity and were dried just before use by refluxing over and distilling from metallic sodium. Pure pentane and hexane were distilled from a suspension of lithium aluminum hydride.

1-Octene, obtained from Coleman and Bell, Division of the Matheson Company, was fractionally distilled through a 30-cm column packed with glass helices, b.p. 122–123°. Indene, a practical grade supplied by the J. T. Baker Company, was similarly redistilled, m.p. $-5$ to $-3°$ and b.p. 181–182°. 1,1-Diphenylethylene was prepared and purified according to the method of Allen and Converse[7]. Bicyclo-[2.2.1]hepta-2,5-diene was redistilled, b.p. 90–91°, after being procured from the Aldrich Chemical Company.

Instrumental analysis employed a Perkin–Elmer Infracord spectrophotometer, a Varian A-60 NMR spectrometer and an F & M Model 720 vapor phase chromatograph. For chromatographic analyses a 10% silicone gum rubber-on-firebrick column and programmed temperature were used. The reported melting points are corrected.

*Reaction of* 1-*octene with triphenylaluminum* (1/1 *ratio*)

A heterogeneous mixture of 5.16 g (0.020 mole) of triphenylaluminum and 2.24 g (0.020 mole) of 1-octene was heated at 125–130° for 24 h at normal pressure and then at 180–200° for 48 h under 0.1 mm Hg pressure (oil-bath temperatures). The volatile material caught in the liquid air trap during the heating period proved to be principally 2-phenyl-1-octene (*cf. infra*).

The viscous reaction residue was dissolved in 25 ml of hexane and 15 ml of water added (gas evolution). To ensure complete hydrolysis, the biphasic system was stirred at a bath temperature of 70–80° for 4 h. Separation of the organic extract and drying over anhydrous calcium sulfate, followed by evaporation of the solvent, yielded a residue containing essentially one product, together with a trace of a minor component (GLC analysis on a 6-ft, 10% silicone gum-rubber column operated at oven temperatures, 70–270° and heated at 10°/min; retention times of 1350 sec (major) and 1410 sec). Distillation gave a 72% of 2-phenyloctane, b.p. 43–45°/0.1 mm. The identity and purity of this compound were established by infrared and NMR spectroscopic analysis. Its neat infrared spectrum was identical with spectrum no. 407 of the American Petroleum Institute Research Project 44 collection[8]. Furthermore, the broad, intense absorption between 725–760 cm$^{-1}$, characteristic of 1-phenyloctane (API no. 337), was absent, so that this isomer could, at most, be only a very minor impurity. Likewise, the lack of a sharp band at 810–820 cm$^{-1}$ rules against the presence of other than traces of 3-phenyloctane[9]. In confirmation of this infrared assignment the NMR spectrum displayed the proper 5/17 ratio of phenyl protons to aliphatic protons and the one-proton, unsymmetrical quintet centered at 3.55 ppm (RR′CHPh).

The distillation of the cold-trap liquid gave a liquid identified as principally 2-phenyl-1-octene contaminated with 2-phenyloctane [infrared bands at 1635 (C=C), 1585 ($C_6H_5C{=}C$) and 900 ($C{=}CH_2$)]. Only a weak band was found at 975 cm$^{-1}$, where a *trans*-CH=CH would be expected to absorb intensely, and no absorption was displayed in the 790–840 cm$^{-1}$ region, where trisubstituted ethylenes would absorb [*viz.*, $CH_3C(C_6H_5){=}CHC_5H_{11}$]. The NMR spectrum displayed a one-proton doublet at 5.2 ppm and a one-proton multiplet (possibly quartet) at 5.02 ppm (both $J \sim 1$ Hz).

*Reaction of* 1,1-*diphenylethylene with triphenylaluminum*

A mixture of 1.8 g (0.010 mole) of 1,1-diphenylethylene and 2.58 g (0.010 mole) of triphenylaluminum was heated at an oil-bath temperature of 210–215° for 42 h. (No reaction was observable under 200°.) After all volatile matter was removed by reducing the pressure to 0.1 mm Hg and heating at 110–120° (bath) for an extended period, the reaction residue was dissolved in 25 ml of ethyl ether and treated with 25 ml of water for 3 h at 50–60°. After usual work-up the organic extract was subjected to GLC analysis; 1,1-diphenylethylene, 1,1-diphenylethane, 1,1,2-triphenylethane and triphenylethylene were detected. Their presence was verified in several ways: by checking the GLC retention times with authentic samples; by observing characteristic $r_f$ values in TLC analysis on silica gel (solvent, pet. ether/$CCl_4$ in 1/1 v/v); by detecting the appropriate proton absorptions in the NMR spectrum of the crude reaction mixture and by separating the products by column chromatography on alumina using petroleum ether (b.p. 30–60°) as the eluting solvent. The same analytical procedures ruled out the presence of 1,1,1-triphenylethane. The relative amounts of 1,1-diphenylethane, 1,1,2-triphenylethane and triphenylethylene were approximately the same and comprised *ca.* 50% of the mixture.

*Reaction of bicyclo*[2.2.1]*hepta*-2,5-*diene with triphenylaluminum*

A solution of 9.2 g (0.10 mole) of bicyclo[2.2.1]hepta-2,5-diene and 5.16 g (0.020 mole) of triphenylaluminum in 20 ml of dry benzene was heated in a bath at 100–110° for 2 h. The reaction solution was then evaporated under reduced pressure (final pressure 0.1 mm Hg) at 60–70°. The cream-yellow solid residue was dissolved in 25 ml of ethyl ether and 25 ml of water added. The resulting mixture was heated with stirring for 4 h at 50° to ensure hydrolysis. The organic extract, obtained after usual work-up, contained two products, as revealed by GLC analysis. One product, obtained by distillation, 2.05 g (60%) at b.p. 94–97°/2.9 mm, was identified as *exo*-5-phenylbicyclo[2.2.1]hept-2-ene[10] on the bais of infrared bands at 3000, 1485, 1325, 740 and 700 $cm^{-1}$ and NMR absorptions characteristic of the phenyl, vinyl, benzylic and aliphatic protons, as well as by its transformation to *exo,exo*-2,5-diphenylbicyclo-[2.2.1]heptane (*cf. infra*).

The other product (1.8 g, 30%) was isolated from the distillation residue and recrystallized from 95% ethanol in the form of white leaflets, m.p. 86–88°. From its NMR spectrum [phenyl singlet at $\delta$ 7.18; triplet at 3.20 (1H); broad peak at 3.52 (1H), multiplet at 1.7–2.0 (2H) and broad singlet at 1.55 (1H)] and its agreement with the properties given in the literature[10], this compound was identified as *exo,exo*-2,5-diphenylbicyclo[2.2.1]heptane.

A run involving 2.75 g (0.030 mole) of diene and 7.0 g (0.027 mole) of triphenylaluminum in refluxing benzene solution for 12 h gave 1.63 g (36%) of the *exo*-5-phenyl product and 3.42 g (51%) of the *exo,exo*-2,5-diphenyl product, m.p. 87–88°.

*Reaction of exo*-5-*phenylbicyclo*[2.2.1]*hept*-2-*ene with triphenylaluminum*

A solution of 2.8 g (0.011 mole) of triphenylaluminum and 1.8 g (0.011 mole) of *exo*-5-phenylbicyclo[2.2.1]hept-2-ene in 20 ml of dry benzene was heated at a bath temperature of 100–110° for 48 h. After removal of volatile matter under reduced pressure (0.1 mm Hg) at 60–70°, the residue was dissolved in ethyl ether and then heated with water at 50–60° for 4 h. Usual work-up provided a dried organic extract displaying one product peak by GLC analysis. Removal of solvent left 1.60 g of crude product melting over the range, 52–70°. From the appearance of the TLC and the NMR spectrum it seemed that two structurally similar components might have been present, possibly *exo,exo*-2,6-diphenylbicyclo[2.2.1]heptane, together with the verified 2,5-isomer. Various attempted chromatographic separations on alumina or silica gel, however, failed to provide a pure sample of this minor component. Several recrystallizations of the crude product from 95% ethanol did afford pure *exo,exo*-2,5-diphenylbicyclo[2.2.1]heptane, m.p. 86–88°, as verified by mixture melting point and NMR data.

### *Reaction of indene with triphenylaluminum*

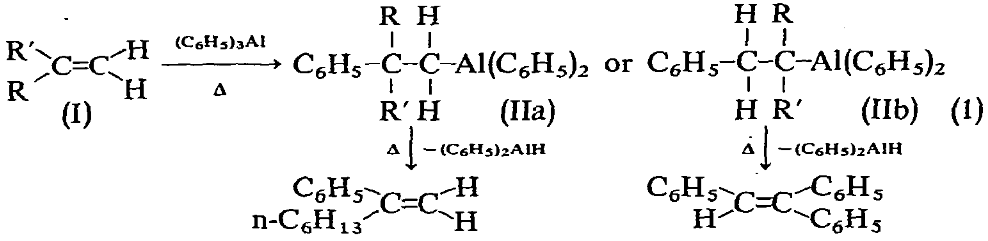
A solution of 7.0 g (0.060 mole) of indene and 2.58 g (0.010 mole) of triphenylaluminum in 25 ml of dry toluene was heated at a bath temperature of 140–150° for 48 h. The volatile material evolved and caught in a dry-ice trap was identified as benzene, 1.63 g [63% of one phenyl equiv. of $(C_6H_5)_3Al$]. Thereupon the reddish-brown solution was subjected to evaporation under reduced pressure and the solid residue dissolved in pentane. Hydrolysis was brought about by adding 25 ml of water and stirring at the reflux temperature for 4 h. After usual work-up and removal of volatile solvent the residual liquid was shown by quantitative GLC analysis to contain 1.7 g of indene (1.5 equiv. of reacted starting material) but no other product of higher retention time.

A run similar to the foregoing was hydrolyzed with deuterium oxide (99.8%). The indene isolated by distillation was shown by NMR analysis to contain at least one deuteron on the five-membered ring (ratio of phenyl protons/cyclopentadienyl protons = 4/2.6 and broadened signals of vinylic and allylic protons).

Finally, a run of the same size and procedure as the first experiment, but without the toluene solvent, was carried out. Distillative work-up of the hydrolyzed reaction residue permitted the isolation of 0.94 g of indene [81%, based upon the reaction of one mole of indene with one mole of $(C_6H_5)_3Al$].

## RESULTS AND DISCUSSION

Triphenylaluminum effected with a wide variation in facility (eqn. 1) the carbalumination of the carbon–carbon double bond of the olefins studied. Based upon the temperature range necessary for addition, the olefin reactivity decreased in the order, bicyclo[2.2.1]hepta-2,5-diene > *exo*-5-phenylbicyclo[2.2.1]hept-2-ene > 1-octene > 1,1-diphenylethylene. Two other reactions accompanied the attempted carbalumination of the olefinic linkage: one was the metallation of acidic carbon–hydrogen bonds; the other was the thermal elimination of substituted aluminum hydride from the carbalumination product. Thus, with indene no carbalumination was realized, but rather metallation leading to diphenyl(indenyl)aluminium took place[11]. At the higher temperatures required for carbalumination some of the product from 1-octene, and much of the product from 1,1-diphenylethylene, underwent loss of diphenylaluminum hydride:



In (Ia), (IIa) $R = n\text{-}C_6H_{13}$, $R' = H$. (III) (IV)
In (Ib), (IIb) $R = R' = C_6H_5$.

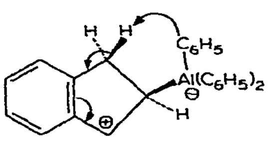
In the reaction with 1-octene the aluminum hydride formed was detected upon hydrolysis; with the 1,1-diphenylethylene the unreacted olefin was hydroluminated by the thermally produced $(C_6H_5)_2AlH$ and hence hydrolysis led to 1,1-diphenylethane.

Except for unreactive olefins like 1,1-diphenylethylene, carbalumination with triphenylaluminum is a feasible manner of adding the elements of $C_6H_5$ and H to an olefinic linkage. An excess of a volatile olefin can be employed because both the unreacted olefin and any phenylated olefin [*e.g.*, (III)] can be removed under reduced pressure from the non-volatile organoaluminum adduct [*e.g.*, (IIa)]. As illustrated by the behavior of bicyclo[2.2.1]hepta-2,5-diene, either the monophenylated product or the diphenylated adduct of certain dienes can be made to predominate under suitable experimental conditions.

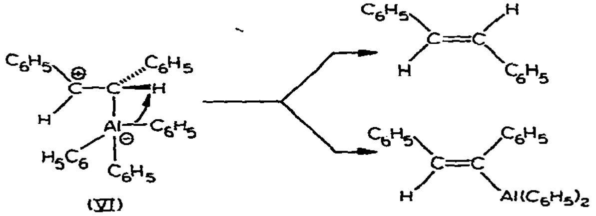
The most interesting aspects of the carbalumination of these olefins by triphenylaluminum are the orientation and stereochemistry of attack. As with aluminum alkyls and terminal olefins[12], the phenyl–aluminum bond was added to 1-octene to yield solely the 2-phenyl-1-alumino adduct (IIa). Although a steric basis might be sought for this regiospecificity[13], the generality of a steric argument breaks down for the case of 1,1-diphenylethylene, where only the reverse mode of addition is observed (IIb). A suitable alternative would be an electronic explanation, whereby triphenylaluminum behaves as an electrophile[14] toward the olefinic linkage. The present results could be interpreted to mean that the direction of such electrophilic attack is determined by the relative stabilities of the two possible products (Hammond's thermic postulate where transition state resembles the product in configuration[15]). Thus, 1-octene yields the primary alumino adduct (more stable than secondary alumino isomer[16]), while 1,1-diphenylethylene forms the tertiary alumino adduct [likely more stable than the (2,2,2-triphenylethyl)aluminum isomer[17]].

The high reactivity, *exo*-phenylation and regiospecificity displayed by the bicyclic olefins are also compatible with attack by electrophilic aluminum[18]. The remarkable regiospecificity of the diphenylation of bicyclo[2.2.1]hepta-2,5-diene, yielding the 2,5-diphenyl adduct as the only observable product, is appealingly consistent with transannular dipolar assistance to electrophilic attack. This explanation requires no recourse to $\pi$-complexation of the reagent on the *endo*-faces of the diene, as proposed by Zeiss and coworkers for a similar phenylation of this diene by triphenylchromium[10].

Finally, the metallation, rather than the carbalumination, of indene is also interpretable as electrophilic attack on the olefinic linkage (V). Support for such



(V)



(VI)

attack can also be adduced from the heating of *cis*-stilbene with triphenylaluminum in refluxing mesitylene and subsequent deuterolysis. A mixture of undeuterated *trans*-stilbene and α-deuterio-*cis*-stilbene was isolated[19]. These results speak for a π- or σ-complex (VI) which can promote isomerization or metallation.

## ACKNOWLEDGEMENTS

The authors are grateful to the Donors of the Petroleum Research Fund and to the National Science Foundation for support of separate phases of this research under Grants PRF-723A and GP-13673, respectively. They are also indebted to Dr. William C. Kaska and Mr. Nicolas E. Burlinson for valuable orienting experiments.

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